DOI: 10.1002/ejic.201200964



The 1,4,5-Triaminotetrazolium Cation (CN₇H₆⁺): A Highly Nitrogen-Rich Moiety

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Dedicated to the memory of Professor Dr. Detlef Schröder

Keywords: Nitrogen heterocycles / Amination / Energetic materials / Structure elucidation

The amination of 1,5-diamino-1,2,3,4-tetrazole with tosylhydroxylamine yielded 1,4,5-triaminotetrazolium tosylate. Metathesis reactions yielded energetic bromide, nitrate, and nitrotetrazolate 2-oxide salts. Owing to the exceedingly high nitrogen content of the cation (>84 % !), the calculated heats of formation and the experimental explosive and thermal

Introduction

Many scientists are attracted to this field as a result of the unique challenges encountered in synthesis and characterization of these prospective replacements for currently used energetic materials. Within the field of energetic materials, nitrogen-rich compounds are extensively looked at as replacements for currently used energetics because they are higher performing and are more environmentally friendly alternatives.^[1–5]

Traditional energetic materials including TNT (2,4,6-trinitrotoluene) and RDX (1,3,5-trinitro1,3,5-triazinane) obtain the majority of their energy content by oxidation of their carbon backbones through the presence of an oxidizer in the molecule. With new research in the development of novel energetics, two new classes of explosive materials have been introduced: those containing either ring or cage strain (e.g., energetic cubanes) and those with high heats of formation that are nitrogen rich (e.g., tetrazoles and tetrazines). These strategies have also been combined to make strained, nitrogen-rich heterocycles a promising and well-investigated area of research.^[6–11]

Among the elements, nitrogen occupies a unique position; the strong, short triple bond means that there is a large energetic driving force towards the formation of mo-

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sensitivities are exceedingly high. For the first time, the X-

lecular nitrogen. In singly and doubly bonded nitrogen systems, this is especially true, where the more contiguous nitrogen atoms in the system leads to higher heats of formation and, as such, higher performances.^[7,8]

Nitrogen-rich heterocycles, especially tetrazoles, have been the backbones of various new explosive compounds, as the carbon position can be easily tailored. This allows the introduction of various substituents to create compounds that span a range of sensitivities from highly sensitive primary explosives to insensitive secondary explosives.^[11,12] However, the tailoring of substituents on the nitrogen atoms of tetrazole rings is far less investigated. Alkvlation reactions are well known;^[13-15] however, the addition of carbon atoms often has negative effects on explosive performance. In our recent work, we reported on a series of N-aminated energetic tetrazoles that were the result of aminating energetic anions with hydroxylamine-O-sulfonic acid.^[16] The N-amination of energetic anions gave neutral N-amino species with very high performances, and in this work, we extended this methodology to the amination of a well-known neutral tetrazole species (1,5-diaminotetrazole) to yield the first energetic tetrazolium cation containing three amino groups on the same tetrazole ring.

The 1,4,5-triaminotetrazolium cation, at over 84% nitrogen, belongs to the unique class of compounds containing over 80% nitrogen.^[8,17,18] Beyond use in explosive materials, compounds containing such high nitrogen contents are important in propellant formulations, as lower reaction temperatures and higher N₂/CO ratios in the combustion products result in lower erosivity. It has been shown that lower erosivity results from the presence of higher concentrations of nitrogen in the combustion gasses of a propellant leading to surface formation of iron nitride instead of iron carbide on the inside of the barrel.^[18]

In this work, we have aminated 1,5-diaminotetrazole with *O*-tosylhydroxylamine to yield 1,4,5-triaminotetrazolium tosylate. Through metathesis reactions, the bromide, nitrate, and nitrotetrazolate 2-oxide salts were all prepared. The compounds were characterized by X-ray diffraction, infrared and Raman spectroscopy, multinuclear NMR spectroscopy, elemental analysis, and differential scanning calorimetry (DSC). Computational calculations confirming the high energetic performance were also performed.

Results and Discussion

Synthesis

O-Tosylhydroxylamine is not stable in storage, so it was prepared from ethyl *O*-*p*-tolylsulfonylacetohydroximate by hydrolysis with 60% perchloric acid (Scheme 1) before each reaction. After hydrolysis, it was then poured into ice water and extracted with dichloromethane, and the dichloromethane solution was dried with sodium sulfate.^[16] A solution of *O*-tosylhydroxylamine (THA) was then added to an acetonitrile solution/suspension of 1,5-diaminotetrazole. After reaction for 3 d, the crude 1,4,5-triaminotetrazolium tosylate was obtained (Scheme 2).

$$\begin{array}{c} \mathsf{H}_{3}\mathsf{C} \\ \mathsf{EtO} \end{array} \xrightarrow{\mathsf{O}-\mathsf{S}^{2+}} \\ \begin{array}{c} \mathsf{O}-\mathsf{S}^{2+} \\ \mathsf{O}^{-} \end{array} \xrightarrow{\mathsf{CH}_{3}} \\ \begin{array}{c} \mathsf{HCIO}_{4} \\ \mathsf{O}^{-} \end{array} \xrightarrow{\mathsf{H}_{2}\mathsf{N}} \\ \begin{array}{c} \mathsf{O}^{-} \\ \mathsf{O}^{-} \end{array} \xrightarrow{\mathsf{CH}_{3}} \\ \begin{array}{c} \mathsf{CH}_{3} \\ \mathsf{O}^{-} \end{array} \xrightarrow{\mathsf{CH}_{3}} \\ \end{array}$$

Scheme 1. Synthesis of *O*-tosylhydroxylamine (THA) from ethyl-*O*-*p*-tolylsulfonylacetohydroximate.



Scheme 2. Synthesis of triaminotetrazolium tosylate.

The as-prepared 1,4,5-triaminotetrazolium tosylate (1) was then dissolved in a minimal amount of ethanol, concentrated hydrobromic acid was added, and 1,4,5-triaminotetrazolium bromide (2) was precipitated by the addition of diethyl ether. Through metathesis reactions with either silver nitrate or silver nitrotetrazolate 2-oxide, 1,4,5-triaminotetrazolium nitrate (3) and 1,4,5-triaminotetrazolium nitrotetrazolate 2-oxide (4) were obtained, respectively (Scheme 3). Crystals were grown of all salts, with the exception of 4, by diffusing ether into a methanolic solution of the salt. Compound 4 was unable to be crystallized despite repeated attempts.



Scheme 3. Metathesis reactions of the 1,4,5-triaminotetrazolium cation.

Spectroscopy

Multinuclear NMR spectroscopy proved to be a useful tool for the characterization of the energetic cation and its salts. In the ¹H NMR spectrum, the 1,4,5-triaminotetrazolium cation shows two resonances. The first at $\delta \approx 8.9$ ppm for the amino group attached to the carbon atom of the tetrazole ring, and another at $\delta \approx 6.9$ ppm for the *N*-amino groups, which is double the intensity of the previous resonance. In the ¹³C NMR spectrum, a single peak for the lone carbon atom is observed at $\delta = 147$ ppm.

The IR and Raman spectra of all compounds were collected and assigned by using frequency analysis from an optimized structure (B3LYP/cc-pVDZ using Gaussian09 software^[19]). All calculations were performed at the DFT level of theory; the gradient-corrected hybrid three-parameter B3LYP^[20,21] functional theory has been used with a correlation consistent p-VDZ basis set.[22-25] The infrared spectra of the triaminotetrazolium cation possesses five strong intensity bands that are easily rendered to medium or low intensity when paired with an anion with strong absorbances. As bromide salt 2 only has resonances resulting from the triaminotetrazolium cation, this spectrum was used extensively for comparison. The calculated spectrum shows a strong absorbance at 922 cm⁻¹ resulting from N-NH₂ wagging. In the spectrum of the bromide salt, this peak is visible at 867 cm^{-1} , and in nitrate salt 3, it appears at 825 cm⁻¹. In the spectra of tosylate 1 and nitrotetrazolate 2-oxide 4, the presence of other peaks in the area makes assignment unclear. The next high-intensity band occurs at 1787 cm⁻¹ in the calculated spectrum and arises from C-N stretching with symmetric C1–N1/C1–N4 ring deformation. In the observed spectra, this band occurs at 1722, 1715, 1726, and 1717 cm^{-1} for compounds 1–4, respectively. The remaining strong bands result from symmetric N-NH₂, symmetric C-NH₂, asymmetric N-NH₂, and asymmetric C-NH₂ N-H stretching at calculated wavenumbers of 3449, 3535, 3537, and 3670 cm⁻¹, respectively. In the observed spectra, these all occur in the range from 3400 to 3000 cm⁻¹ and show a greater deviation between the experimental and calculated values compared to the previous bands. The calculated Raman spectrum of the triaminotetrazolium cation contains one very high-intensity peak at 779 cm⁻¹ resulting

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from tetrazole ring breathing. In the spectra of 2 and 3, this signal occurs at 789 and 791 cm⁻¹, respectively. In the spectra of 1 and 4, the presence of multiple peaks in this region precludes exact assignment.

Single-Crystal X-ray Analysis

With the exception of nitrotetrazolate 2-oxide salt 4, all compounds were characterized by X-ray crystallography. Table 1 summarizes a selection of crystallographic data and refinement details. Exact bond lengths and angles of the 1,4,5-triaminotetrazolium cations are given in Table 2. The bond lengths and angles within the tetrazole moiety are comparable to those in 1,5-diaminotetrazole,[26] with several small changes. We will discuss the changes based on bond lengths and angles from salt 1; however, the trend also holds for salt 3. The tetrazole ring within 1,5-diaminotetrazole is not symmetric; C1-N1 is longer than C1-N4: 1.345 vs. 1.327 Å, respectively. After amination, these bond lengths, while they become similar at 1.344 and 1.332 Å, respectively, they do not become equivalent, leaving the tetrazole ring slightly distorted. Concurrently, N2-N3 and N3–N4 increase in length from 1.363 to 1.376 Å. Finally, of note is that only the protons of the C1–NH₂ are planar with the ring, indicating electronic communication between the π system of the ring and the p electrons on the N5 amino group. The process of amination reduces electron density within the tetrazole ring, easily explaining why the C1-N5 bond length decreases to 1.314 Å from the 1.334 Å seen in 1,5-diaminotetrazole. The N-NH2 bond lengths, N1-N6 and N4-N7, do not change appreciably from the N-NH₂ bond length in 1,5-diaminotetrazole.

Table 1. Crystallographic data and structure refinement details for triaminotetrazolium salts.

	1.0.5MeOH	3
Formula	C ₁₇ H ₃₀ N ₁₄ O ₇ S ₂	CH ₆ N ₈ O ₃
FW [gmol ⁻¹]	606.67	320.23
Crystal system	triclinic	orthorhombic
Space Group	$P\overline{1}$	$Pna2_1$
<i>a</i> [Å]	6.5993(2)	7.7144(18)
<i>b</i> [Å]	13.6361(5)	17.605(4)
<i>c</i> [Å]	15.9896(6)	5.2393(13)
a [°]	90.705(3)	90
β [°]	95.737(3)	90
γ [°]	98.577(3)	90
V[Å ³]	1415.12(9)	711.6(3)
Ζ	2	4
$\rho_{\rm calcd.} [\rm g cm^{-3}]$	1.424	1.663
T [K]	173	173
R_1/wR_2 (all data)	0.0549/0.0969	0.0440/0.0736
$R_1/wR_2 \ (I > 2\sigma)$	0.0381/0.0881	0.0360/0.0696
S _c	1.048	1.049

Salt 1.0.5MeOH crystallizes in the triclinic space group $P\bar{1}$ with four formula units in the unit cell and a density of 1.424 g cm⁻³. The asymmetric unit consists of two anion-cation pairings and one methanol molecule that is shown in Figure 1.

Fable 2. Crystallographic	e bond lengths and	angles of the	1,4,5-tri-
aminotetrazolium cation	s in the structures	of 1 and 3 .	

	1a	1b	3
A–B length [Å]	·	
C1–N1	1.344(2)	1.334(2)	1.338(4)
C1-N4	1.332(2)	1.339(2)	1.342(3)
C1-N5	1.314(2)	1.313(2)	1.308(4)
N1-N2	1.376(2)	1.376(2)	1.381(3)
N2-N3	1.277(3)	1.277(3)	1.271(3)
N3-N4	1.376(2)	1.375(2)	1.374(3)
N1-N6	1.386(2)	1.381(2)	1.385(3)
N4-N7	1.384(2)	1.392(2)	1.374(3)
A-B-C angle [°]		
C1-N1-N2	110.33(16)	110.30(17)	110.1(2)
C1-N4-N3	110.85(16)	110.40(17)	110.5(2)
C1-N1-N6	124.36(17)	124.23(17)	122.8(2)
C1-N4-N7	123.82(17)	123.45(17)	124.1(2)
N1-C1-N4	103.79(17)	104.14(17)	103.9(2)
N5-C1-N1	128.60(19)	128.38(19)	127.4(2)
N5-C1-N4	127.61(19)	127.47(19)	128.7(3)



Figure 1. View of the asymmetric unit in the structure of 1.0.5 MeOH. Ellipsoids are drawn at the 50% probability level.

The crystal structure of **2** could not be determined sufficiently due to a hard twinning problem. By using a twin data reduction, two species could be detected and separated. One of them^[27] could be solved and refined to yield a final wR_2 value of 23.2%. However, it was not possible to locate any electron density for the hydrogen atoms.

Salt **3** crystallizes in the non-centrosymmetric orthorhombic space group $Pna2_1$ with four formula units in the unit cell. The molecular moiety is shown in Figure 2. Although an intensive hydrogen-bonding network is formed, the density is only 1.663 gcm⁻³. This is quite low in comparison to other tetrazolium compounds, especially the corresponding 5-aminotetrazolium nitrate $(1.847 \text{ g cm}^{-3})^{[28]}$ and 1,5-diaminotetrazolium nitrate $(1.727 \text{ g cm}^{-3})^{.[29]}$ Interestingly, the density decreases by increasing the number of amino groups connected to the tetrazolium ring nitrogen atoms.



Figure 2. Molecular unit of **3**. Ellipsoids are drawn at the 50% probability level.

Hydrogen bonding takes place at all oxygen atoms of the nitrate anion and all hydrogen atoms of the 1,4,5-triamino-tetrazolium cations, which is indicated in Figure 3.



Figure 3. The unit cell of 4, depicting the important hydrogen bonds of the nitrate anion.

Energetic Properties

Calculation of the heats of formation of compounds **2–4** was performed by using the atomization method based on CBS-4M calculated gas-phase enthalpies and Equation (1) described recently in detail.^[5]

$$\Delta_{\rm f} H^{\circ}_{\rm (g,M,298)} = H_{\rm (molecule,298)} - \Sigma H^{\circ}_{\rm (atoms,298)} + \Sigma \Delta_{\rm f} H^{\circ}_{\rm (atoms,298)}$$
(1)

The results are depicted in Table 3. The gas-phase heat of formation $[\Delta_{\rm f} H^{\circ}({\rm g},{\rm M})]$ was converted into the solid-state heat of formation $[\Delta_{\rm f} H^{\circ}({\rm s})]$ (Table 3) by using the Jenkins and Glasser equations for the lattice energies and enthalpies.^[30] The gas-phase enthalpies of formation of Br⁻ (-239.5 kJ mol⁻¹) and NO₃⁻ (-313.6 kJ mol⁻¹) fit very well to experimentally obtained values published in the literature (Br⁻ -233.9 kJ mol⁻¹)^[31] and NO₃⁻ (-300.2 kJ mol⁻¹).^[32]

Table 3. CBS-4M results and gas-phase enthalpies.

$\begin{array}{c ccccccccccccccccccccccccccccccccccc$				
$\begin{array}{cccccccccccccccccccccccccccccccccccc$		Formula	- <i>H</i> ²⁹⁸ [a.u.]	$\Delta_{\rm f} H({\rm g}) \\ [{\rm kJ}{\rm mol}^{-1}]$
4 $C_2H_6N_{12}O_3$ 1212.0 ^[a]	1,4,5-TAT ⁺ Br ⁻ NO ₃ ⁻ NTX ⁻ 2 3	$\begin{array}{c} CH_{6}N_{7}^{+} \\ Br^{-} \\ NO_{3}^{-} \\ CN_{5}O_{3}^{-} \\ CH_{6}N_{7}Br \\ CH_{6}N_{8}O_{3} \end{array}$	424.051319 2572.763437 280.080446 536.798772	1129.0 -239.5 -313.6 83.0 889.5 ^[a] 815.4 ^[a]
	4	$C_2H_6N_{12}O_3$		1212.0 ^[a]

[a] Gas-phase	enthalpies	of formatio	n of the i	onic compo	ounds are
taken as the r	espective sur	ms of the no	on-interact	ting compo	nent ions.

These molar standard enthalpies of formation $(\Delta H_{\rm m})$ were used to calculate the molar solid-state energies of formation $(\Delta U_{\rm m})$ according to Equation (2) (Table 3).

$$\Delta U_{\rm m} = \Delta H_{\rm m} - \Delta n R T \tag{2}$$

where Δn is the change of mol of gaseous components.

As it can be seen from Table 4, compounds 2-4 are formed endothermically. The most positive value of 722.6 kJ mol⁻¹ is obtained for 4 as a result of its highly energetic and endothermic anion. The calculation of the detonation parameters was performed with the program EX-PLO5.05^[33] by using the X-ray density for 3 and a helium gas pycnometer density for 4. The results for 3 and 4 in comparison to those of RDX are gathered in Table 5.

Table 4. Calculation of the solid-state energies of formation ($\Delta_f U^\circ$).

	2	3	4
$V_{\rm M} [{\rm nm^3}]$	0.167	0.178	0.234 ^[a]
$U_{\rm L}$ [kJ mol ⁻¹]	606.7	520.9	484.5
$\Delta H_{\rm L}$ [kJ mol ⁻¹]	607.9	525.9	489.5
$\Delta_{\rm f} H^{\circ}({\rm s}) [{\rm kJ} {\rm mol}^{-1}]$	281.6	289.5	722.6
Δn	6.5	8.5	10.5
$\Delta_{\rm f} U^{\circ}({\rm s}) [{\rm kJ} {\rm kg}^{-1}]$	1518.4	1743.2	3040.6

[[]a] The molecular volume of **4** was recalculated from the X-ray structure of ammonium 5-nitrotetrazolate N-oxide^[5] and a literature value for the nitrate anion.^[29]

The detonation parameters of **3** and **4** are slightly lower than those of RDX, which is due to their lower densities. However, the detonation velocities (V_{det}) of 8779 m s⁻¹ (for **3**) and 8872 m s⁻¹ (for **4**) are much higher than those of TNT ($V_{det} = 7459 \text{ m s}^{-1}$) and also PETN (pentaerythritol tetranitrate) ($V_{det} = 8561 \text{ m s}^{-1}$) calculated by using the same approaches. With respect to a potential use as propellant ingredients, **3** and **4** show very high values for the specific impulse (using 60 bar chamber pressure isobaric rocket conditions) of 260 s (for **3**) and 259 s (for **4**).

In addition, the sensitivities towards shock, friction, and electrostatic discharge were carried out for all compounds. Generally, tosylate salt 1 was found to be the least sensitive with 10 J and 240 N friction and impact sensitivities, respectively, classifying it as a "less sensitive"^[36] energetic material. For remaining compounds 2–4, all impact energies were 2 J or less and all friction sensitivities were below 10 N. Of interest is the very high sensitivities of bromide salt 2, uncharacteristic for an energetic cation paired with a non-energetic anion; for example, triaminoguanidinium

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Table 5. Energetic properties of 3 and 4 in comparison to those of RDX.

	3	4	RDX
Formula	CH ₆ N ₈ O ₃	C ₂ H ₆ N ₁₂ O ₃	C ₃ H ₆ N ₆ O ₆
FW [gmol ⁻¹]	178.11	246.15	222.12
Impact sensitivity [J] ^[a]	2	1	7.5 ^[34]
Friction sensitivity [N] ^[b]	5	7	120[34]
ESD-test [J] ^[c]	0.050	0.100	0.2
N [%] ^[d]	62.91	68.28	37.84
$\Omega \left[\%\right]^{[e]}$	-17.96	-26.00	-21.61
$T_{\rm dec}$ [°C] ^[f]	78	84	210
Density [gcm ⁻³] ^[g]	1.663	1.71	1.858 (90 K) ^[35]
$\Delta_f U^{\text{o}} [\text{kJ} \text{kg}^{-1}]^{[\text{h}]}$	1743.2	3040.6	489.0
EXPLO5.05 Values			
$-\Delta_{\rm Fx} U^{\circ}[\rm kJkg^{-1}]^{[i]}$	5745	5910	6190
$T_{\rm det} [\rm K]^{[j]}$	4006	4221	4232
$P_{\rm CI}$ [kbar] ^[k]	311	326	380
$V_{\rm det} [{\rm ms^{-1}}]^{[1]}$	8779	8872	8983
$V_{0} [L kg^{-1}]^{[m]}$	876	815	734
<i>I</i> _S [s] ^[n]	260	259	258

[a] Impact sensitivity [BAM drophammer (1 of 6)]. [b] Friction sensitivity [BAM friction tester (1 of 6)]. [c] Electrostatic discharge device (OZM research). [d] Nitrogen content. [e] Oxygen balance $[\Omega = (xO - 2yC - 1/2zH)M/1600]$. [f] Decomposition temperature from DSC ($\beta = 5$ °C). [g] From X-ray diffraction. [h] Calculated energy of formation. [i] Energy of explosion. [j] Explosion temperature. [k] Detonation pressure. [l] Detonation velocity. [m] Volume of detonation gases (assuming only gaseous products). [n] Specific impulse using isobaric (60 bar) conditions.

bromide is insensitive.^[37] Bromide salt **2** is highly sensitive towards mechanical stimuli (impact, friction), but with 15 mJ electrostatic sensitivity it is also capable of being initiated by a static charge created by the human body. All these results indicate that the 1,4,5-triaminotetrazolium cation is far too sensitive towards mechanical and electrostatic stimuli to find any practical use as an energetic material.

Finally, compounds **2–4** all decompose in the range from 102 to 78 °C. These thermal stabilities are too low for a practical energetic material; however, it does provide insight that there is a limit on the thermal stability as heats of formation and associated nitrogen content increase.

Conclusions

The amination of 1,5-diaminotetrazole with *O*-tosylhydroxylamine is an effective method of preparing the new energetic 1,4,5-tetrazolium cation. Metathesis reactions allowed easy preparation of the bromide, nitrate, and nitrotetrazolate 2-oxide salts. The crystal structure of this unique cation was determined for the first time, as were its spectral properties. The energetic performances of the nitrate and nitrotetrazolate 2-oxide salts were calculated, illustrating the ability of the triaminotetrazolium cation to form highperformance energetic materials almost on par with RDX. However, the major limitations of the triaminotetrazolium cation are its sensitivities; the mechanical, electrostatic, and thermal sensitivities of this new energetic cation are all far too low to be used in practical energetic materials.

Experimental Section

General Methods: All reagents and solvents were used as received (Sigma-Aldrich, Fluka, Acros Organics) if not stated otherwise. Op-Tolylsulfonylacetohydroximate was prepared according to a literature procedure.^[12] Melting and decomposition points were measured with a Linseis PT10 DSC by using heating rates of 5 °Cmin⁻¹. ¹H NMR and ¹³C NMR spectra were measured with a JEOL instrument. All chemical shifts are quoted in ppm relative to TMS (1H, 13C). Infrared spectra were measured with a Perkin-Elmer FTIR Spektrum BXII instrument equipped with a Smith Dura SampIIR II ATR-unit. Transmittance values are described as strong (s), medium (m), and weak (w). Mass spectra were measured with a JEOL MStation JMS 700 instrument. Raman spectra were measured with a Perkin-Elmer Spektrum 2000R NIR FT-Raman instrument equipped with a Nd:YAG laser (1064 nm). The intensities are reported as percentages of the most intensive peak and are given in parentheses. Elemental analyses were performed with a Netsch STA 429 simultaneous thermal analyzer. Sensitivity data were determined by using a BAM drophammer and a BAM friction tester. The electrostatic sensitivity tests were carried out by using an Electric Spark Tester ESD 2010 EN (OZM Research) operating with the "Winspark 1.15" software package.

CCDC-896690 (for 1.0.5MeOH) and -896691 (for 3) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

CAUTION! The described compounds are energetic materials with sensitivity to various stimuli. Although we encountered no issues in the handling of these materials, proper protective measures (face shield, ear protection, body armor, Kevlar gloves, and earthened equipment) should be used at all times.

1,4,5-Triaminotetrazolium Tosylate (1): Ethyl O-p-tolylsulfonylacetohydroximate (3.5 g, 13.6 mmol) was slurried in 60% perchloric acid (40 mL) and stirred for 2 h. The mixture was then poured into ice water (500 mL) and once the ice had melted the solution was extracted with dichloromethane (5×50 mL). The dichloromethane solutions were combined and dried with sodium sulfate. This was then added to a solution of 1,5-diaminotetrazole (1.0 g, 9.99 mmol) in acetonitrile (100 mL), and the mixture was stirred for 3 d. The solution was then evaporated to yield the crude triaminotetrazolium tosylate (2.74 g, 95%). IR: $\tilde{v} = 3348$ (w), 3278 (m), 3186 (m), 3047 (m), 2861 (w), 1722 (m), 1652 (w), 1625 (w), 1602 (w), 1496 (w), 1403 (w), 1340 (w), 1177 (s), 1123 (s), 1136 (m), 1010 (m), 898 (m), 821 (m), 793 (m), 712 (w), 682 (m) cm⁻¹. Raman (1064 nm) = 3277 (4), 3190 (7), 3066 (49), 3032 (4), 2986 (5), 2924 (15), 2870 (4), 2739 (4), 2698 (4), 2575 (5), 1734 (4), 1599 (34), 1575 (4), 1524 (5), 1495 (3), 1456 (1), 1446 (3), 1391 (20), 1309 (4), 1212 (12), 1192 (20), 1128 (84), 1042 (39), 1015 (16), 902 (4), 802 (98), 687 (9), 638 (38), 616 (11), 555 (9), 492 (6), 400 (14), 367 (3), 348 (7), 314 (3), 296 (35), 230 (17) cm⁻¹. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.95 (s, 2 H, C-NH₂), 7.47 (d, ${}^{3}J_{H,H}$ = 8 Hz, 2 H, Ar C-H OTs-), 7.11 (d, ${}^{3}J_{H,H}$ = 8 Hz, 2 H, Ar C-H OTs-) 6.94 (s, 4 H, N-NH₂), 2.28 (s, 3 H, CH₃) ppm. ¹³C NMR (68 MHz, $[D_6]DMSO$): $\delta = 147.1$ (s, 1 C, CN7H6), 146.1, 138.3, 128.6, 126.0, 21.3 (tosylate carbon atoms) ppm. MS (FAB+): m/z = 116.1 [CN₇H₆]. MS (FAB-): m/z= $170.0 [C_7H_7SO_3]$. BAM impact: 10 J. BAM friction: 240 N.

1,4,5-Triaminotetrazolium Bromide (2): To a solution of triaminotetrazolium tosylate (0.25 g, 0.87 mmol) dissolved in a minimal amount of ethanol was added 47% hydrobromic acid (0.21 g). The mixture was stirred for 5 min and then diethyl ether (50 mL) was added, which resulted in the precipitation of triaminotetrazolium



bromide(0.15 g, 88%). DSC: 102 °C (dec.). IR: $\tilde{v} = 3350$ (w), 3210 (m), 3067 (m), 1715 (s), 1685 (m), 1654 (w), 1600 (m), 1576 (w), 1560 (m), 1541 (w), 1394 (w), 1214 (m), 1192 (m), 1134 (w), 1091 (m), 1015 (m), 927 (w), 867 (s), 789 (w), 769 (w), 700 (w), 671 (w) cm⁻¹. Raman (1064 nm) = 3250 (11), 3218 (1), 3202 (1), 3180 (1), 3147 (1), 3117 (1), 1731 (2), 1599 (9), 1521 (2), 1412 (2), 1384 (25), 1319 (1), 1223 (3), 1136 (4), 1093 (12), 1010 (5), 790 (100), 636 91), 617 (20), 545 (3), 474 (3), 351 (2), 303 (22) cm⁻¹. ¹H NMR (400 MHz, [D₆]DMSO): $\delta = 8.96$ (s, 2 H, C-NH₂), 6.99 (s, 4 H, N-NH₂) ppm. ¹³C NMR (68 MHz, [D₆]DMSO): $\delta = = 147.2$ (s, 1 C, CN₇H₆) ppm. MS (FAB+): *m/z* = 116.1 [CN₇H₆]. MS (FAB-): *m/z* = 78.9 [Br]. CN₇H₆Br (196.01): calcd: C 6.13, H 3.09, N 50.02; found too sensitive for measurement. BAM impact: <1 J. BAM friction: <5 N. ESD: 0.015 J.

1,4,5-Triaminotetrazolium Nitrate (3): To a solution of triaminotetrazolium bromide (0.300 g, 1.53 mmol) dissolved in distilled water (10 mL) was added a solution of silver nitrate (0.260 g, 1.53 mmol) in distilled water (10 mL). The solution was stirred in the dark at 100 °C for 3 h. After filtration of silver bromide and evaporation of the aqueous filtrate, triaminotetrazolium nitrate (0.250 g, 92%) was obtained. DSC: 78 °C (dec.). IR: $\tilde{v} = 3325$ (m), 3200 (m), 3088 (m), 1726 (m), 1645 (m), 1621 (m), 1374 (s), 1311 (s), 1220 (m), 1125 (w), 1086 (m) 1048 (w), 1033 (w), 1009 (w), 949 (w), 863 (w), 825 (m), 791 (w), 719 (w), 683 (w) cm⁻¹. Raman (1064 nm) = 3325 (1), 3214 (10), 1734 (2), 1620 (6), 1583 (2), 1521(2), 1413 (1), 1384 (31), 1332 (1), 1231 (1), 1128 (3), 1088 (11), 1050 (100), 1009 (2), 792 (84), 722 (5), 617 (20), 543 (1), 323 (11), 291 (2) cm⁻¹. ¹H NMR (400 MHz, [D₆]DMSO): δ = 8.97 (s, 2 H, C- $NH_2),\ 7.00$ (s, 4 H, $N{-}NH_2)$ ppm. ^{13}C NMR (68 MHz, $[D_6]{-}$ DMSO): $\delta = 147.2$ (s, 1C, CN₇H₆) MS (FAB+): m/z = 116.1 $[CN_7H_6]$. MS (FAB-): $m/z = 62.0 [NO_3]$. $CN_7H_6NO_3$ (178.11): calcd: C 6.74, H 3.40, N 62.91; found too sensitive for measurement. BAM impact: 2 J. BAM friction: 5 N. ESD: 0.050 J.

1,4,5-Triaminotetrazolium Nitrotetrazolate 2-Oxide (4): To a solution of triaminotetrazolium bromide (0.200 g, 1.02 mmol) dissolved in distilled water (10 mL) was added silver nitrotetrazolate 2-oxide (0.243 g, 1.02 mmol). The solution was stirred in the dark at 100 °C for 3 h. After filtration of silver bromide and evaporation of the aqueous filtrate, triaminotetrazolium nitrotetrazolate 2-oxide (0.668 g, 67%) was obtained. DSC: 84 °C (dec.). IR: $\tilde{v} = 3384$ (m), 3338 (m), 3188 (m), 2951 (m), 1717 (m), 1636 (w), 1535 (s), 1466 (m), 1457 (m), 1419 (s), 1391 (s), 1311 (s), 1234 (m), 1185 (w), 1129 (w), 1114 (w), 1085 (w), 1051 (w), 1001 (w), 917 (w), 846 (w), 785 (s), 759 (w), 693 (w) cm⁻¹. Raman (1064 nm): = 3382 (1), 3313 (1), 3251 (5), 1831 (1), 1599 (1), 1544 (5), 1522 (2), 1430 (100), 1407 (37), 1317 (19), 1237 (3), 1087 (77), 1059 (21), 1004 (94), 851 (1), 797 (11), 762 (2), 617 (6), 491 (4), 429 (2), 399 (1), 340 (8), 239 (7) cm⁻¹. MS (FAB+): m/z = 116.1 [CN₇H₆]. MS (FAB-): m/z =62.0 [NO₃]. CN₇H₆CN₅O₃ (246.15): calcd: C 9.76, H 2.46, N 68.28; found too sensitive for measurement. BAM impact: 1 J; BAM friction: 7 N; ESD: 0.100 J.

Acknowledgments

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL), the Armament Research, Development and Engineering Center (ARDEC), the Strategic Environmental Research and Development Program (SERDP), and the Office of Naval Research (ONR Global, title: "Synthesis and Characterization of New High Energy Dense Oxidizers (HEDO) - NICOP Effort ") under contract nos. W911NF-09-2-0018 (ARL), W911NF-09-1-0120 (ARDEC), W011NF-09-1-0056 (ARDEC), and 10 WPSEED01-002/WPI765 (SERDP) is gratefully acknowledged. The authors acknowledge collaborations with Dr. Mila Krupka (OZM Research, Czech Republic) in the development of new testing and evaluation methods for energetic materials and with Dr. Muhamed Sucesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen, Proving Ground, MD) and Mr. Gary Chen (ARDEC, Picatinny Arsenal, NJ) for many helpful and inspired discussions and support of our work. The authors want to thank St. Huber for measuring the sensitivities.

- [1] K. O. Christie, Propellants Explos. Pyrotech. 2007, 32, 194-204.
- [2] Y.-H. Joo, J. M. Shreeve, Angew. Chem. 2009, 121, 572–575; Angew. Chem. Int. Ed. 2009, 48, 564–567.
- [3] D. E. Chavez, D. A. Parrish, Propellants Explos. Pyrotech. 2012, DOI: 10.1002/prep.201100112.
- [4] O. S. Bushuyev, P. Brown, A. Maiti, R. H. Geen, G. R. Peterson, B. L. Hope-Weeks, L. J. Hope-Weeks, J. Am. Chem. Soc. 2012, 134, 1422–1425.
- [5] M. Göbel, K. Karaghiosoff, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, J. Am. Chem. Soc. 2010, 132, 17216–17226.
- [6] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Chem. Eur. J.* 2011, 17, 13068–13077.
- [7] Y.-C. Li, C. Qi, S.-H. Li, H.-J. Zhang, C.-H. Sun, Y.-Z. Yu, S.-P. Pang, J. Am. Chem. Soc. 2010, 132, 12172–12173.
- [8] T. M. Klapötke, D. G. Piercey, *Inorg. Chem.* 2011, 50, 2732– 2734.
- [9] P. Carlqvist, H. Östmark, T. Brinck, J. Phys. Chem. A 2004, 108, 7463–7467.
- [10] T. Schroer, R. Haiges, S. Schneider, K. O. Christie, *Chem. Commun.* 2005, 1607–1609.
- [11] J. Fronabarger, M. D. Williams, W. B. Sanborn, J. G. Bragg, D. A. Parrish, M. Bichay, *Propellants Explos. Pyrotech.* 2011, 36, 541–550.
- [12] N. Fischer, T. M. Klapötke, D. G. Piercey, J. Stierstorfer, Z. Anorg. Allg. Chem. 2012, 638, 302–310.
- [13] T. M. Klapötke, C. M. Sabate, J. Stierstorfer, New J. Chem. 2009, 33, 136–147.
- [14] N. Fischer, K. Karaghiosoff, T. M. Klapötke, J. Stierstorfer, Z. Anorg. Allg. Chem. 2010, 636, 735–749.
- [15] R. Boese, T. M. Klapötke, P. Mayer, V. Verma, Propellants Explos. Pyrotech. 2006, 31, 263–268.
- [16] T. M. Klapötke, D. G. Piercey, J. Stierstorfer, *Dalton Trans.* 2012, 41, 9451–9459.
- [17] M. H. V. Huynh, M. A. Hiskey, D. E. Chavez, R. D. Gilardi, J. Am. Chem. Soc. 2005, 127, 12537–12543.
- [18] T. M. Klapötke, J. Stierstorfer, J. Am. Chem. Soc. 2009, 131, 1122–1134.
- [19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, Gaussian 09, Revision A.1, Gaussian, Inc., Wallingford, CT, 2009.

[20] A. D. Becke, J. Chem. Phys. 1993, 98, 5648-5652.

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- [21] C. Lee, W. Yang, R. G. Parr, Phys. Rev. B 1988, 37, 785-789.
- [22] D. E. Woon, T. H. Dunning Jr, R. J. Harrison, J. Chem. Phys. 1993, 98, 1358–1371.
- [23] R. A. Kendall, T. H. Dunning Jr, R. J. Harrison, J. Chem. Phys. 1992, 96, 6796–6806.
- [24] T. H. Dunning Jr, J. Chem. Phys. 1989, 90, 1007-1023.
- [25] K. A. Peterson, D. E. Woon, T. H. Dunning Jr., J. Chem. Phys. 1994, 100, 7410–7415.
- [26] A. S. Lyakhov, P. N. Gaponik, S. V. Voitekhovich, Acta Crystallogr., Sect. C 2001, 57, 185–186.
- [27] Cell parameters for **2**: $P2_1/n$, a = 8.178(2) Å, b = 5.4205(9) Å, c = 15.169(2) Å, $\beta = 96.225(19)^\circ$, V = 668.5(2) Å³, Z = 2, $\rho = 1.888$ g cm⁻³.
- [28] M. von Denffer, T. M. Klapötke, G. Kramer, G. Spieß, J. M. Welch, *Propellants Explos. Pyrotech.* 2005, 30, 191–195.
- [29] J. C. Galvez-Ruiz, G. Holl, K. Karaghiosoff, T. M. Klapötke, K. Löhnwitz, P. Mayer, H. Nöth, K. Polborn, C. J. Rohbogner, M. Suter, J. J. Weigand, *Inorg. Chem.* 2005, 44, 4237–4253.
- [30] a) H. D. B. Jenkins, H. K. Roobottom, J. Passmore, L. Glasser, *Inorg. Chem.* **1999**, *38*, 3609–3620; b) H. D. B. Jenkins, D. Tudela, L. Glasser, *Inorg. Chem.* **2002**, *41*, 2364–2367; c) H. D. B. Jenkins, L. Glasser, *Inorg. Chem.* **2002**, *41*, 4378–88.

- [31] D. A. Johnson in Some Thermodynamic Aspects of Inorganic Chemistry, 2nd ed., Cambridge University Press, Ambridge, 1982.
- [32] a) J. A. Davidson, F. C. Fehsenfeld, C. J. Howard, Int. J. Chem. Kinet. 1977, 9, 17; b) D. A. Dixon, D. Feller, C.-G. Zhan, J. S. Francisco, Int. J. Mass Spectrom. 2003, 227, 421–438.
- [33] a) M. Sućeska, *EXPLO5.05 Program*, Zagreb, Croatia, 2011;
 b) M. Sućeska, *Propellants Explos. Pyrotech.* 1991, 16, 197–202.
- [34] R. Mayer, J. Köhler, A. Homburg, *Explosives*, 5th ed., Wiley-VCH, Weinheim, 2002.
- [35] P. Hakey, W. Ouellette, J. Zubieta, T. Korter, Acta Crystallogr., Sect. E 2008, 64, 01428.
- [36] Impact: Insensitive >40 J, less sensitive ≥35 J, sensitive ≥4 J, very sensitive ≤3 J; friction: insensitive >360 N, less sensitive = 360 N, sensitive <360 and >80 N, very sensitive ≤80 N, extremely sensitive ≤10 N. According to the UN Recommendations on the Transport of Dangerous Goods.
- [37] T. M. Klapötke, unpublished results.

Received: August 22, 2012 Published Online: October 5, 2012